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FLUX PINNING AND PROPERTIES OF SOLID-SOLUTION $(Y,Nd)_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ SUPERCONDUCTORS (PREPRINT)

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14. ABSTRACT
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ABSTRACT

The effect of chemical composition variations on the flux pinning and physical properties of $(Y,Nd)_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ superconductors was studied in powders processed by solid-state reaction and equilibrated in air at 910 °C. An extended region of single-phase assemblages was determined for compounds with Ba = 2.0 to 1.7 and Nd = 0 to 1.3. At 77 K, Ba substituted and $(Y_{0.2}Nd_{0.8})Ba_2Cu_3O_{7-\delta}$ compounds had enhanced pinning properties (normalized $J_c(H)$) than other compositions tested including $YBa_2Cu_3O_{7-\delta}$. At 65 K, all compounds had similar pinning as Y123 (Nd = 0), except for composition $(Y_{0.3}Nd_{0.6})Ba_{1.9}Cu_3O_{7-\delta}$ which had reduced pinning. For increasing Nd and decreasing Ba (< 2.0), the T_c and J_c were reduced for the processing conditions tested.

INTRODUCTION

Copper based (Rare-Earth)$Ba_2Cu_3O_{7-z}$ (RE123) superconductors are being considered for applications including thin film coated conductors and bulk devices because of their high superconducting transition temperatures (T_c) > 92 K, and high critical current density (J_c) at 77 K in useful magnetic fields. While these materials have many desirable attributes at 77 K, it is of interest to increase the J_c in applied magnetic fields even further by increasing the flux pinning properties of the superconductor. Many methods can be considered to introduce flux pinning defects into the superconductors, including irradiation and introduction of second-phase defects or precipitates. One method used particularly for bulk applications is to substitute rare-earth cations into the RE123 compound. Many variations of this theme have been studied, including substitution in (Y,R)123 with R = Ho, Dy, Gd, Eu, and Pr, and various other combinations of rare-earths such as (Gd,Sm,Eu)123 [1-15]. Possible mechanisms by which such substitutions increase the flux pinning include: **(a)** addition of second-phase defects by precipitation or composition changes, **(b)** formation of finely distributed lower T_c components from the mixed solubility of RE with Ba and intersolubility of RE or other mechanisms, or **(c)** randomly distributed oxygen-deficient zones which have lower T_cs [7,8]. The finely distributed lower T_c components are suggested as a cause of the so-called 'fishtail' effect, where as the magnetic field is increased, the J_c increases as the lower T_c components transition to normal behavior before the J_c decreases at much higher applied magnetic fields [7,8]. The peak of J_c maximum in these materials typically occurs at applied fields of about 2 T to 3 T.

Studies of the system $(Y_{1-x}Nd_x)Ba_2Cu_3O_{7-\delta}$ have, to our knowledge, been limited thus far to melt-processed or single crystal materials [9-14], and powders [15]. Single crystals in this system demonstrated very high J_c and the 'fish-tail' effect for Nd content varying from 0.1 to 0.4 after varying oxygenation treatments [13].

In this paper, the effect of composition changes in $(Y,Nd)_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ is studied in solid-state powders annealed in air to achieve chemical equilibrium. The powders prepared in this work are expected to have different properties than (Y,Nd)123 melt-processed or crystals in previous studies, where non-equilibrium processes can affect the physical properties. In melt-processed materials it is almost impossible to eliminate the formation of second-phase defects such as RE211, which can affect pinning. With powder processing, it possible to completely eliminate second-phase defects, and investigate other causes of pinning more related to the intrinsic properties of the crystal structure.

For the studies herein, powders were annealed in air, which may have an advantage for flux pinning by increasing the substitution of Nd onto the Ba site, and causing lower T_c solid-solutions to form [8,15,16]. While further treatments of the powders in varying O_2 pressures is predicted to improve the superconductivity and possibly increase the fish-tail effect, such treatment may decrease the pinning effect by reducing substitution of Nd onto the Ba site. The effects of annealing in air are studied in this paper to examine the role of chemical substitution prior to oxygen treatments. This paper also provides J_c and flux pinning results for $(Y,Nd)_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ for a large range of compositions, including Ba < 2.0.

EXPERIMENTAL**

Superconducting powders were prepared by the solid-state reaction method, using starting reactants of Nd_2O_3, Y_2O_3, $BaCO_3$, and CuO (≥ 99.95% purity). The powders were dehydrated at 450 °C prior to weighing. The powders were mixed and ground with mortar and pestle, calcined by slow heating 650 °C to 850 °C at 25 °C/h, and subsequently annealed with intermediate grinding at 880 °C and 910 °C. Powders were annealed at 910 °C with intermediate grinding until phase equilibrium was reached (3-4 annealings), as determined by X-ray diffraction (XRD). The powders were reacted in ~1 cm diameter pellets (0.5 g to 1 g batches), formed by lightly pressing ($5\text{-}10 \times 10^6$ Pa) in molds. X-ray diffraction was performed with a Rigaku diffractometer. A step size of 0.03° was used for the θ-2θ scans.

Superconducting properties of powders were measured with a SQUID magnetometer (Quantum Design**, MPMS/$MPMS^2$). Magnetization-applied field (M-H) hysteresis loops at different temperatures were made by heating samples to 100 K and zero-field cooling (ZFC) to the measurement temperature. The magnetic J_c was estimated using the extended Bean critical current model $J_c = 15(\Delta M)/R$ where ΔM is the volume magnetization, and R is the radius of the superconducting volume roughly approximated as 0.00005 cm for the finely reacted powders [17].

Field-cooled (FC) Meissner and zero-field-cooled (ZFC) measurements were performed from 5 K to 100 K [17]. The SQUID magnet was reset to zero before any measurements. The superconducting volume percentages were calculated using $\chi(\%) = 4\pi\chi_v/(1-D^*4\pi\chi_v)$, where $\chi_v = M/H_{appl}$ is the measured magnetic susceptibility, and D = 1/3 is the demagnetization factor assuming a spherical particle distribution [17]. The applied magnetic field was $H_{appl} = 796$ A/m - H_{rem}, where H_{rem} is the remnant field of the magnet after resetting to zero, determined for each sample by measuring M(H) from 796 A/m to -398 A/m at 79.6 A/m intervals and plotting when M = 0 (± 8 A/m accuracy). The transition temperature of the largest volume fraction of powder was determined by finding the temperature when $(d^2\chi/dT^2) \cong 0$ upon cooling from 100 K. The standard uncertainty of T_c measurements was 0.5 K, as determined from both ZFC and FC curves and multiple measurements. The standard uncertainty of Meissner volume fractions was ± 5%, as determined from multiple measurements of one sample. The standard uncertainty of J_cs was measured using differences of ΔM for both positive and negative applied fields. Standard uncertainties for normalized $J_c(H)$ curves were calculated by measuring errors of ΔM for positive and negative applied fields, and averaging the ΔM errors over the range of approximately 0.1 T to 4.8 T.

** Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the Air Force Research Laboratory or the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

RESULTS

The range of compositions studied is shown in Figure 1. All of the compositions were nominal single-phase as determined by XRD, in agreement with previous results [15], except for a small region (Ba = 2.0 and Y = 0.3 to 0.4). For this small region, it was not possible to reach the single-phase composition within ~ 3 grinding and annealing cycles at 910 °C, and secondary phases including $BaCuO_{2+x}$ were observed to remain in the composite. Rather than achieving a new equilibrium phase assemblage, it is probable that reaction kinetics were too slow for these compositions, and higher temperatures might be required to form the single-phase assemblage.

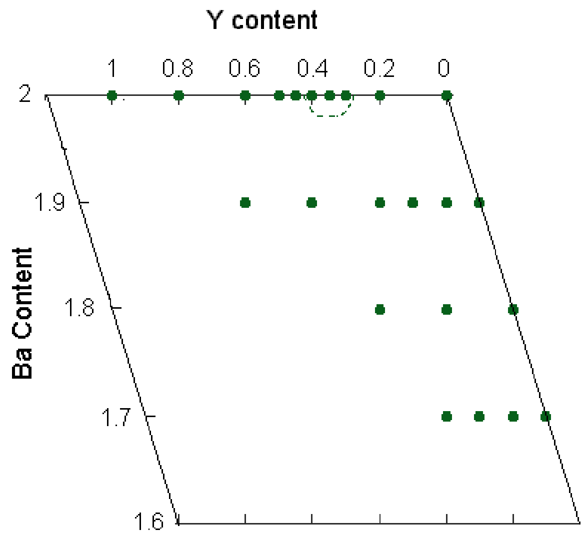

Figure 1. Compositions of $(Y,Nd)_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ studied. All compositions were nominal single-phase, excluding Ba = 2 and Y = 0.3 to 0.4.

The superconducting transitions of Ba = 2.0 compositions are shown in Figure 2. The transitions were broadened for Nd > 0.4, and the transition for the largest volume fraction of the powder was reduced to ~ 73 K for the Nd = 1.0 composition. A reduction and broadening of T_c for the Nd = 1.0 composition is usually observed without further processing in reduced oxygen partial pressures [15,16]. The transition of the bulk component for different compositions is shown in Figure 3. With increasing Nd and reduced Ba content, the T_c of the bulk powder is decreased, in agreement with trends reported previously for $(Y,Nd)_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ and single-phase $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ [15,16]. Assuming previous optimization methods can be applied, it's possible T_cs for the Nd-rich compositions can be increased and sharpened by further processing in reduced O_2 atmosphere [7,8,15,16].

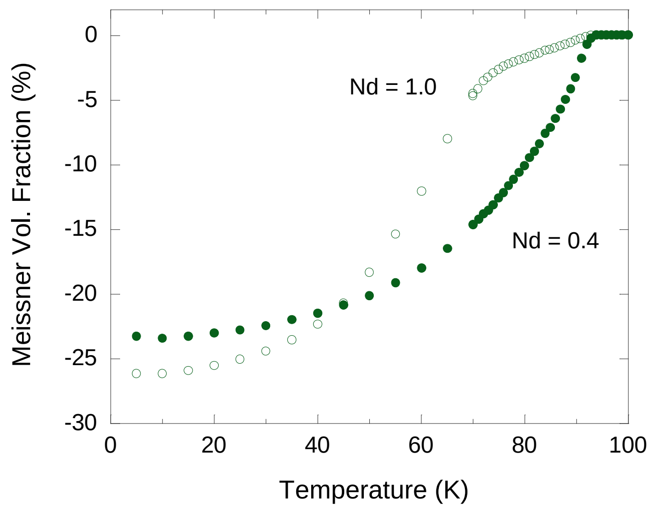

Figure 2. Meissner volume fraction (%) for Ba = 2.0 and different Nd content.

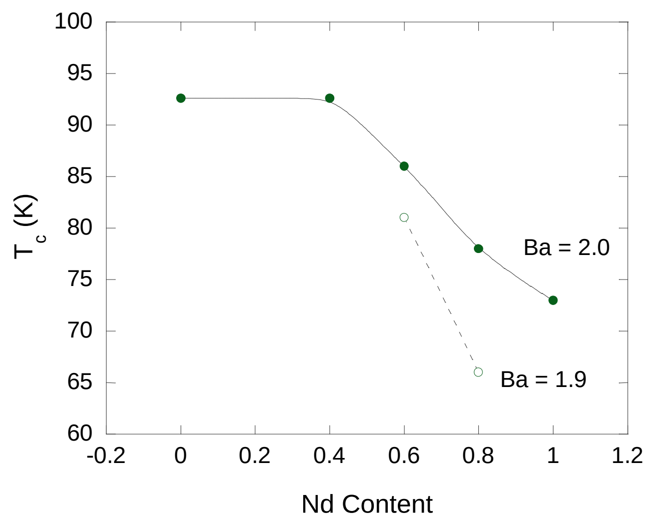

Figure 3. Transition temperature of the bulk superconducting volume fraction.

Figure 4 plots the maximum J_cs of the powders for different composition and temperature. In general, the J_cs decreased with increasing Nd substitution. For Nd > 0.4, the reduction of J_c is probably related to the reduction of T_c as shown in Figures 2 and 3. For Nd = 0.4, an intrinsic drop of J_c is suggested, as the T_cs were similar to the Nd = 0 compound. The trend of decreasing J_c with increasing

Nd substitution has not been published elsewhere in the literature, to our knowledge. The decrease of J_c for Nd = 1.0 (Nd123) compared to Nd = 0.0 (Y123) is consistent with overall trends reported for thin films: at 77 K Nd123 $J_c \cong 3$ MA/cm^2 compared to Y123 $J_c \cong 6$-9 MA/cm^2 [18,19].

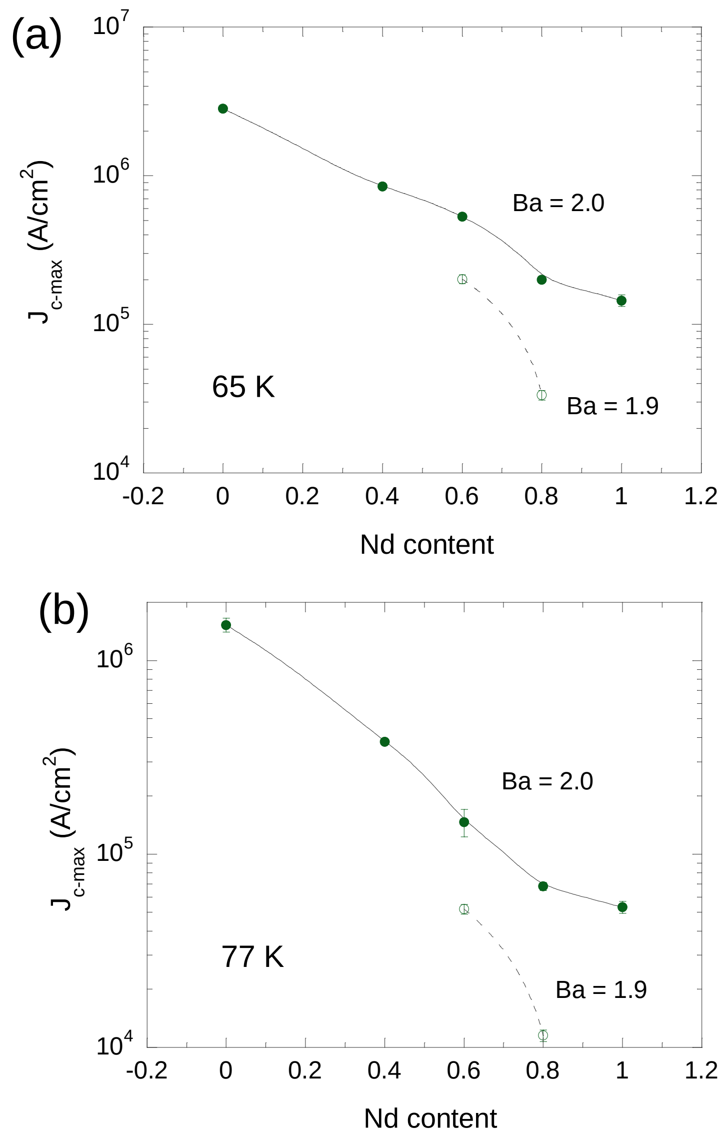

Figure 4. Maximum critical current density estimated from M-H loops at $H_{appl} \sim$ 0.06 T to 0.1 T for varying Ba and Nd content.

The effect of applied magnetic field on J_c for varying compositions is shown in Figure 5. At 77 K, the Ba substituted and Nd = 0.8 compounds had enhanced pinning properties (normalized $J_c(H)$) than other compositions tested.

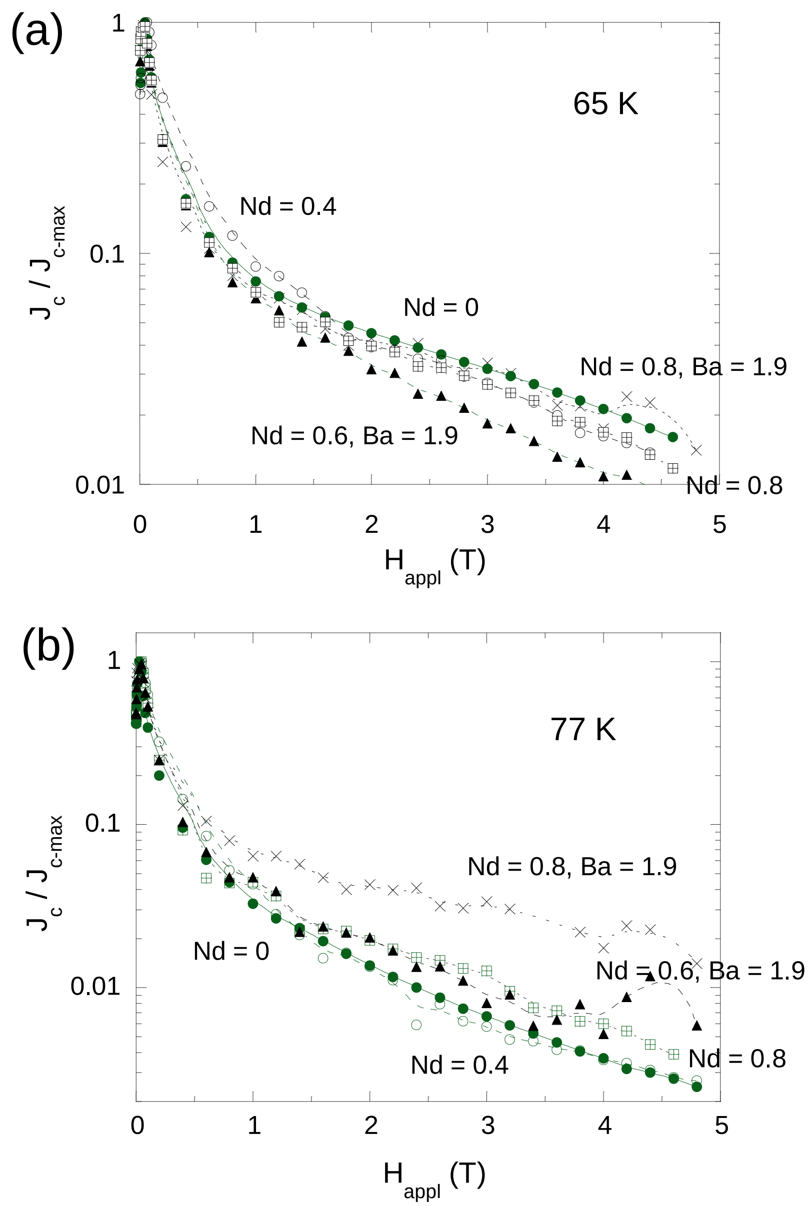

Figure 5. Normalized ($J_c/J_{c\text{-max}}$) for Ba = 2.0 and varying Nd content. The standard uncertainties of $J_c(H)$ measurements were at 65 K = ± 2.5%, ± 2%, ± 11 %, ± 5%, ± 8.5%, and at 77 K = ± 6%, ± 3.5%, ± 9%, ± 7.5%, ± 9.5%, for Nd = 0, 0.4, 0.8, and Nd = 0.6 Ba = 1.9 and Nd = 0.8 Ba = 1.9 compositions respectively.

The enhanced pinning at 77 K may be caused by lower T_c components intimately mixed with the high T_c material, or changes in the intrinsic crystal structure or other mechanisms. At 65 K, the Nd and Ba substituted compounds had similar pinning as Y123 (Nd = 0), except for one composition (Nd = 0.6, Ba = 1.9) which had reduced pinning. At 65 K and 77 K, the powders showed a very small fish-tail effect, with $J_{c\text{-}max}$ occurring at 0.06 T to 0.1 T depending on composition. By comparison, the peak of maximum J_c in oxygenated melt-processed materials usually occurs around 2 to 3 T [7,8]. This suggests the powder compositions in this work are homogeneous in nature without the oxygen-deficient regions thought to cause the fish-tail effect [7,8]. A homogenous distribution of oxygen is expected as a consequence of the small size of the powders, and the near-equilibrium conditions used for processing.

CONCLUSIONS

The flux pinning and physical properties of $(Y,Nd)_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ powders annealed in air to achieve single-phase equilibrium were studied for varying compositions. At 77 K, Ba substituted and $(Y_{0.2}Nd_{0.8})Ba_2Cu_3O_{7-\delta}$ compounds had higher values of normalized $J_c(H)$ than other compositions tested, including $YBa_2Cu_3O_{7-\delta}$. At 65 K, all compounds had similar pinning as Y123 (Nd = 0), except for composition $(Y_{0.3}Nd_{0.6})Ba_{1.9}Cu_3O_{7-\delta}$ which had reduced pinning. With increasing Nd substitution and reduced Ba content (< 2.0), the T_c and J_c were reduced for the processing conditions tested, consistent with trends in the literature. While processing in air is generally considered to lower T_c transitions for Nd-rich 123 compounds, the results here show that improvements of pinning can be made for partial substitution of Y with Nd and Ba.

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